



Cu-exchanged Al-rich SSZ-13 zeolite from organotemplate-free synthesis as NH₃-SCR catalyst: Effects of Na⁺ ions on the activity and hydrothermal stability

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ABSTRACT

The relatively low activity at lower temperatures and high cost of SSZ-13 zeolite from organotemplate synthesis are two of major problems of presently commercialized Cu-SSZ-13 catalysts for NH₃-SCR reaction. Cu-exchanged Al-rich SSZ-13 catalysts with Si/Al = 4 from organotemplate-free synthesis have been prepared, and show superior NH₃-SCR performance with NO conversions above 85% at wide-temperature window ranging from 150 to 650 °C. Cu-Na-SSZ-13 catalysts with varied amount of residual Na⁺ were prepared by partial ion-exchange of as-prepared Al-rich Na-SSZ-13, and it's found that Cu-Na-SSZ-13 catalyst with moderate Na⁺ content can improve both the low-temperature activity and its hydrothermal stability. ²⁷Al and ¹H MAS NMR spectra indicate that residual Na⁺ can stabilize the framework Al in Al-rich SSZ-13 zeolite. UV-Vis-NIR and H₂-TPR spectra demonstrate that Na⁺ co-cations enhance the reducibility of Cu²⁺, whereas too much amount of Na⁺ may result in the formation of CuO_x during the hydrothermal treatment, and further decrease the hydrothermal stability of Cu-Na-SSZ-13 catalyst. The optimized organotemplate-free Cu-Na-SSZ-13 with 2.7 wt% Cu and 1.7 wt% Na exhibits almost the same NO conversions as the commercial high-silica Cu-SSZ-13 catalyst at 150–550 °C after 750 and 800 °C hydrothermal aging, and shows promising practical applications.

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1. Introduction

Cu-SSZ-13 catalyst with excellent catalytic performance and hydrothermal stability has been commercialized in NH₃-SCR of NO_x for diesel engine exhaust after-treatment [1–4]. With more and more stringent restriction on engine exhaust, enhancing the low-temperature NH₃-SCR activity, especially under 200 °C, is still highly desirable [5–7]. Generally, isolated Cu²⁺ ions locating at the ion-exchange sites in SSZ-13 zeolite act as the active center for NH₃-

SCR reaction, and the amount of isolated Cu²⁺ directly determines the low-temperature activity [8–11]. In fact, the amount of isolated Cu²⁺ is largely dependent on the amount of framework Al and Cu/Al ratio in SSZ-13 zeolite [12]. It's reported that two-Al in 6-membered ring (6MR) of SSZ-13 is the energetically favorable site to accommodate isolated Cu²⁺, though some Cu(OH)⁺ species also populate in the CHA cages near 8MR windows [13–15]. For high-silica SSZ-13 zeolite the available ion-exchange site is rather limited, and increase of Cu content will inevitably result in the aggregated Cu species, which may lead to nonselective oxidation of ammonia at high temperature and further decrease the high-temperature activity [16,17]. Therefore, Al-rich SSZ-13 zeolite offering a large amount of ion-exchange sites and stabilizing the copper ions is highly desirable. Indeed, Al-rich SSZ-13 zeolites with Si/Al ratio

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of 4–7.5 were synthesized using highly cost N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH) or relatively low cost Cu^{2+} coordinated tetra-ethylenepentamine (CuTEPA) as the structure-directing agent (SDA), and the resulted Cu/Al-rich SSZ-13 catalysts showed good catalytic performances in NH_3 -SCR reaction [18–21]. However, both methods use a large amount of organic templates which significantly increases the cost of catalyst and also brings some pollutions from calcination of organic templates. Even though Cu/SSZ-13 catalyst with Si/Al \approx 4 can be readily prepared in one-pot using relatively cheap CuTEPA, a large amount of Cu ions are introduced in the system, tedious post-treatments are still needed to lower the amount of Cu in the zeolite [19,22]. Therefore, using Al-rich SSZ-13 zeolite synthesized from organotemplate-free approach is highly desirable for both saving the cost and environmentally benign manufacture of Cu-SSZ-13 catalyst.

A critical factor for the successful commercialization of high-silica Cu-SSZ-13 (Si/Al = 15–18) catalyst is due to its excellent hydrothermal stability, however, in H-type Al-rich SSZ-13 zeolite, it's found that Al is very susceptible to dealumination [5,23,24]. The hydrothermal stability of Al-rich Cu-SSZ-13 becomes a major problem for practical applications. Recently, certain amount of Na^+ stabilized Al-rich Cu-SSZ-13 (Si/Al = 4–6) catalysts have been reported by different groups, showing improved high- and low-temperature activity and hydrothermal stability in NH_3 -SCR [21,22]. With respect to the effect of Na^+ on the hydrothermal stability of Al-rich Cu-SSZ-13 catalyst, two opposite phenomena were observed. For one-pot synthesized Cu-SSZ-13 (Si/Al = 4) catalyst, it's found after post-treatment with dilute HNO_3 residual Na^+ is detrimental to the hydrothermal stability [22], while Gao et al. [21] found that introduction of certain amount of Na^+ or Li^+ in Cu-SSZ-13 (Si/Al = 6) may be beneficial for the hydrothermal stability. Although the poor hydrothermal stability for one-pot synthesized Cu-SSZ-13 is attributed to the poor stability of Cu ions due to excess amount of Na^+ , the post-treatment by dilute HNO_3 solution may inevitably introduce silanol defects in SSZ-13 zeolite, which may also affect its hydrothermal stability significantly [22,25,26]. Thus, the impact of residual Na^+ on the activity and hydrothermal stability of Al-rich Cu-CHA catalyst is still open, and a systematic investigation is of great importance for its potential application in NH_3 -SCR of NO_x .

In the present study, Al-rich SSZ-13 zeolite from the organotemplate-free synthesis has been employed as the support to host the copper ions at the exchange sites, which shows excellent performances in NH_3 -SCR reaction compared with the commercial high-silica Cu-SSZ-13 catalyst. At the same time, the effects of Na^+ ions on the catalytic activity as well as the hydrothermal stability are systematically studied by varying the amount of residual Na^+ . The microstructure-activity correlation has been revealed by detailed characterizations of resulted catalysts using XRD, UV-Vis-NIR, H_2 -TPR, ^{27}Al and ^1H MAS NMR approaches.

2. Experimental

2.1. Catalyst preparation

Al-rich Na-SSZ-13 zeolite (Si/Al = 4) was synthesized from organotemplate-free approach, and provided by BASF, Germany. In brief, conventional Al-containing SSZ-13 ([Al]-SSZ-13) as seed crystals was hydrothermally synthesized at 150 °C for 5 days by using TMAdaOH as the SDA in the presence of NaOH. Organotemplate-free synthesis of Al-rich SSZ-13 zeolite was carried out in a rotating autoclave (20 rpm) using an amorphous aluminosilicate gel at 170 °C for 2–3 days in the presence of 10–15 wt% calcined CHA zeolite seeds. Fumed silica (Cab-O-Sil M5, Cabot) and NaAlO_2 were used as a silica source and an aluminum source, respectively. The molar

ratio in gel was $20\text{SiO}_2/1\text{Al}_2\text{O}_3/8\text{Na}_2\text{O}/1200\text{H}_2\text{O}$. The obtained product was recovered by filtration, washed with deionized water, and dried at 110 °C. This material was ion-exchanged twice with 0.1 M NH_4NO_3 at 80 °C to mostly remove Na^+ ions to get NH_4 -SSZ-13. Na- NH_4 -SSZ-13 zeolites with different amount of residue Na^+ were prepared by ion exchange of as-prepared Na-SSZ-13 with NH_4NO_3 concentration ranging from 0.005 to 0.02 M at 40 °C. Then, copper ions were introduced by the ion-exchange of NH_4 -SSZ-13 or Na- NH_4 -SSZ-13 with aqueous solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ with different concentrations ranging from 0.004 to 0.007 M at 40 °C. Thereafter, the zeolite slurries were filtered, washed with deionized water and dried at 110 °C overnight. Subsequently, the samples were calcined in muffle oven at 500 °C for 5 h with a ramping rate of 2 °C/min.

For comparison, the conventional commercial Na-SSZ-13 zeolites from organotemplate synthesis (Si/Al = 15, from BASF, Germany) were also employed using the identical preparation procedures. The catalysts were denoted as (m)Cu-(n)Na-SSZ-13-(x) where m and n (wt%) stand for the Cu and Na contents, respectively, and x indicates the Si/Al ratios. For the hydrothermal treatment, the Cu-SSZ-13 catalysts were aged in 10% $\text{H}_2\text{O}/\text{Air}$ at 750 °C or 800 °C for 5 h.

2.2. Catalyst characterization

Cu and Na contents of the resulted catalysts were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2000 DV, USA).

X-ray diffraction (XRD) analysis was carried out on a X-ray diffractometer (Rigaku D-Max Rotaflex) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). UV-Vis-NIR diffuse reflectance spectra were recorded in the range of 190–1400 nm on an Agilent Cary-5000 spectrometer.

H_2 temperature-programmed reduction (TPR) experiments were performed on Micromeritics AutoChem II 2920 chemisorption analyzer. About 50 mg samples were loaded and pretreated under Ar at 300 °C for 1 h to remove adsorbed CO_2 and H_2O . After cooling down to 30 °C, 5% H_2/Ar as the reducing gas was introduced at a flow rate of 50 ml/min, and the temperature was ramped to 650 °C at 10 °C/min.

NH_3 temperature-programmed desorption (NH_3 -TPD) was carried out using an online mass spectrometer (Pfeiffer Omini-star, GSD-320) to detect the effluent gases. Before the measurements, the sample (35 mg) was pretreated in He stream at 450 °C and cooled down to the desired temperatures. 1000 ppm NH_3 in N_2 (100 ml/min) was introduced at 100 °C for 0.5 h, followed by He purging for 1.5 h, then the temperature was ramped from 100 to 650 °C at a rate of 10 °C/min.

All solid-state MAS NMR experiments were performed on Agilent DD2–500 MHz spectrometer. ^1H and ^{27}Al MAS NMR spectra were acquired at 499.8 and 130.2 MHz using a 4 mm MAS NMR probe with a spinning rate of 10 and 14 kHz, respectively. ^1H MAS NMR spectra were recorded using a pulse width of 2.5 μs for a $\pi/2$ pulse, and 64 scans were accumulated with a 4 s recycle delay. Chemical shifts were referenced to tetramethylsilane (TMS). Before ^1H MAS NMR measurement, all samples were dehydrated at 450 °C under a vacuum of $\sim 10^{-4}$ Pa for 16 h. ^{27}Al MAS NMR spectra were accumulated for 400 scans with $\pi/12$ flip angle, and 1 s recycle delay. Chemical shifts were referenced to 1% $\text{Al}(\text{NO}_3)_3$ aqueous solution. ^{27}Al MQ MAS NMR spectra were collected using a three-pulse sequence incorporating a z-filter [27,28].

2.3. Catalytic reaction tests

NH_3 -SCR activity measurements were carried out in a fixed-bed quartz reactor (i.d. 5 mm) with the reactant gas mixture contain-

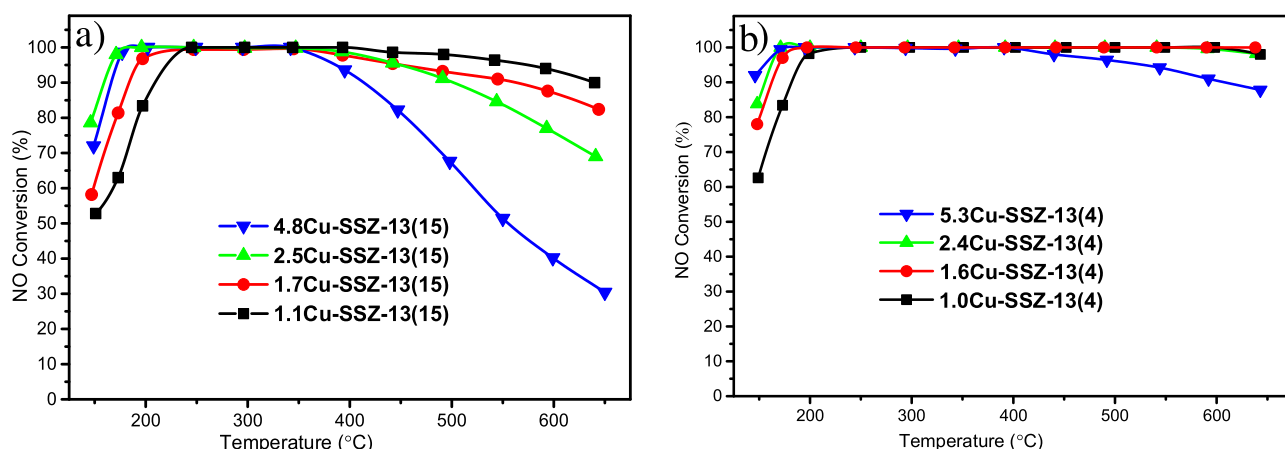


Fig. 1. NO conversions as a function of temperature on Cu-SSZ-13(15) (a) and Cu-SSZ-13(4) (b) series catalysts. Reaction Conditions: 500 ppm NO, 500 ppm NH₃, 10% O₂, 5 vol.% H₂O, balance N₂; GHSV = 80,000 h⁻¹.

ing 500 ppm NO, 500 ppm NH₃, 10% O₂, 5% H₂O, and balance N₂. The total flow rate was 240 ml/min, corresponding to a gas hourly space velocity (GHSV) of 80,000 h⁻¹. NO, NO₂, and N₂O contents were monitored continuously using a chemiluminescence analyzer (ECO Physics CLD60, Switzerland) and an infrared absorption spectrometer (Sick Maihak S710, Germany). To avoid errors caused by the conversion of ammonia in the analyzer, an ammonia trap containing phosphoric acid solution was installed upstream. All data were obtained when the SCR reaction reached the steady state at each temperature.

3. Results

3.1. Effects of Si/Al ratios and Na⁺ ions on NH₃-SCR activity

Fig. 1 depicts NH₃-SCR activities of Cu-SSZ-13 catalysts varying Cu loadings and Si/Al ratios. Na⁺ contents are less than 0.1 wt% in all catalysts and their effects could be ignored. Both high-silica Cu-SSZ-13(15) (Fig. 1a) and Al-rich Cu-SSZ-13(4) (Fig. 1b) catalysts show enhancement of low-temperature activity with the increase of Cu loadings. At high temperature above 400 °C, NO conversions decrease obviously with increase of Cu loadings for high-silica Cu-SSZ-13(15) catalysts. The significant difference between Al-rich and conventional high-silica SSZ-13 supports is that the Al-rich Cu-SSZ-13(4) catalysts maintain excellent high-temperature activity even with Cu loading up to 5.3%. Moreover, even with similar Cu loading, Cu(2.4)-SSZ-13(4) shows superior NH₃-SCR activity with almost 100% NO conversion at broad temperature window ranging from 175 to 650 °C in the presence of 5 vol.% H₂O. In contrast, the conventional Cu(2.5)-SSZ-13(15), i.e. the commercialized Cu-SSZ-13 catalyst, shows relatively lower NO conversion at low temperature 150 °C, and especially, NO conversion decreases from 100% to about 70% when reaction temperature is elevated from 350 to 650 °C. At the same time, Al-rich Cu-SSZ-13(4) catalysts also show good N₂ selectivity with N₂O yield less than 15 ppm at the whole temperature range (Fig. S1 in supplementary material). It can be concluded that Al-rich Cu-SSZ-13(4) is very beneficial for both high- and low-temperature activities in NH₃-SCR reaction, and shows very promising practical applications.

When Al-rich Na-SSZ-13 zeolite from organotemplate-free synthesis was transformed into H-SSZ-13, there is significant amount of extra-framework Al at ~2 ppm and distorted four-coordinated Al at ~40 ppm (Fig. S2 in supplementary material) [23]. It seems that Na⁺ ions could stabilize the framework Al in Al-rich SSZ-13 zeolite during the high temperature calcination. Herein, Al-rich Cu-SSZ-13 catalysts with different amount of residual Na⁺ ions and similar

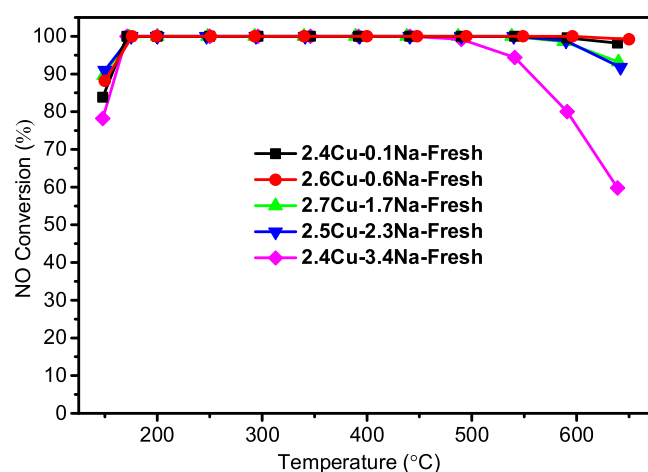


Fig. 2. NO conversions as a function of temperature on fresh Al-rich Cu-Na-SSZ-13(4) series catalysts with different amount of Na⁺ ions. Reaction Conditions: 500 ppm NO, 500 ppm NH₃, 10% O₂, 5% H₂O, balance N₂; GHSV = 80,000 h⁻¹.

Cu content were prepared and evaluated in NH₃-SCR reaction. As shown in Fig. 2, all the as-prepared catalysts show very excellent activity except for the 2.4Cu-3.4Na-SSZ-13(4) catalyst. NO conversions at 150 °C increase slightly from 84% to 91% with Na⁺ content increase from 0.1% to 2.3%. When the temperature is elevated to 650 °C, NO conversions decrease from 100% to 60% with Na⁺ content increasing from 0.1 to 3.4%. The maximum NO conversion at 150 °C is about 90% for 2.5Cu-2.3Na-SSZ-13(4) and 2.7Cu-1.7Na-SSZ-13(4) catalysts with medium Na⁺ content, which also maintain very good high-temperature activities. These results indicate that Na⁺ content should be at moderate level, which has a balance of good low- and high-temperature NH₃-SCR activity.

3.2. Hydrothermal stability

The effect of Na⁺ on the hydrothermal stabilities of (m)Cu-(n)Na-SSZ-13 catalysts are further investigated with corresponding NH₃-SCR activities shown in Fig. 3. After hydrothermal treatment at 750 °C for 5 h, all aged catalysts show different degrees of activity loss at both low and high temperatures compared with fresh catalysts. For aged catalysts NO conversions at 150 °C increase from 63% to 81% when residual Na⁺ content is elevated from 0.1 to 2.3%, whereas the high-temperature activities show the reversed trend. However, for the catalyst with highest Na⁺ content i.e. 2.4Cu-3.4Na-SSZ-13(4) shows much severe degradation of activity in the whole

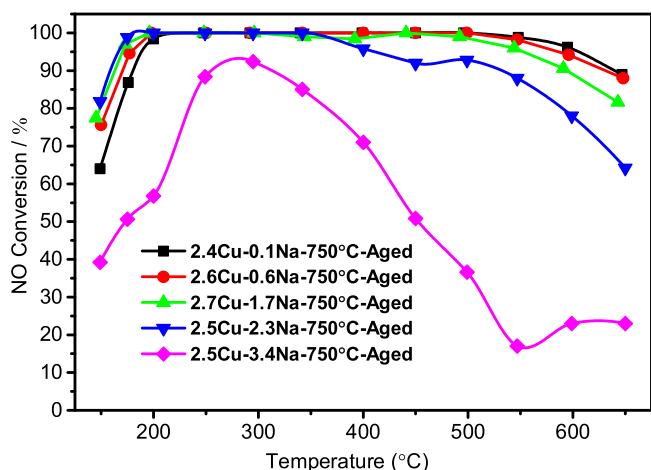


Fig. 3. NO conversions as a function of temperature on hydrothermally aged Al-rich Cu-Na-SSZ-13(4) series catalysts with different amount of Na^+ ions. Reaction Conditions: 500 ppm NO, 500 ppm NH_3 , 10% O_2 , 5% H_2O , balance N_2 ; GHSV = 80,000 h^{-1} .

temperature range. It's worth noting that after hydrothermal aging 2.4Cu-0.1Na-SSZ-13(4) with the lowest Na^+ content shows about 20% and 15% decrease of NO conversion at 150 and 175 °C, respectively, although it has the best high-temperature activities above 550 °C. These results also indicate that Na^+ content should be at a moderate level i.e. 2.7Cu-1.7Na-SSZ-13(4) catalyst has a balance of good low- and high-temperature NH_3 -SCR activity after hydrothermal aging.

It is clear that the optimized catalyst is Al-rich 2.7Cu-1.7Na-SSZ-13(4), which is also compared with the commercial high-silica 2.5Cu-SSZ-13(15) after different stages of hydrothermal treatments (Fig. 4). For the fresh catalysts, the as-prepared 2.7Cu-1.7Na-SSZ-13(4) shows significantly better NO conversion in both low and high temperature ranges. After 750 °C hydrothermal aging, 2.7Cu-1.7Na-SSZ-13(4) still shows better performance from 150 to 550 °C, although there is activity enhancement at higher temperatures for the commercial 2.5Cu-SSZ-13(15) catalyst above 500 °C due to the re-dispersion of Cu species after hydrothermal aging [29]. With much sever hydrothermal aging at 800 °C for another 5 h, 2.7Cu-1.7Na-SSZ-13(4) also shows similar NH_3 -SCR activity to the commercial 2.5Cu-SSZ-13(15) from the normal reaction-temperature window of 150–550 °C although its activity decreases even promptly above 600 °C. Moreover, all the fresh and aged 2.7Cu-1.7Na-SSZ-13(4) catalysts show similar N_2 selectivity to 2.5Cu-SSZ-13(15) with very little N_2O yield (Fig. S3 in supplementary material). Nevertheless, in practical applications the loss of high-temperature activities above 600 °C in Na^+ stabilized Cu-SSZ-13(4) after hydrothermal aging should be still taken into consideration in the depletion of particulate matter (dePM) process for diesel particulate filters (DPF).

3.3. Characterizations of fresh and aged Cu-Na-SSZ-13 catalysts

XRD patterns of the fresh and hydrothermally aged Al-rich Cu-Na-SSZ-13 catalysts with different amount of residual Na^+ ions are shown in Fig. 5. There is no obvious difference for the fresh catalysts (Fig. 5a). However, after 750 °C hydrothermal aging, significant decrease of peak intensities is observed for 2.4Cu-3.4Na-SSZ-13 (Fig. 5b). XRD results indicate that catalysts with Na^+ content up to 2.3% can still maintain the long-range order crystallinity of zeolite after 750 °C hydrothermal aging. ^{27}Al MAS NMR was carried out to demonstrate the effect of Na^+ ions on the stability of framework Al in Al-rich SSZ-13, and the spectra are shown in Fig. 6. For the fresh catalysts in Fig. 6a, the main signals are resulted

from four-coordinated framework Al at 58 ppm, while there are minor signals of five- and six-coordinated extra-framework Al near 35 ppm and –2 ppm, respectively. The spectra also indicate a weak trend that extra-framework Al at –2 ppm increase with the decrease of Na^+ content. After 750 °C hydrothermal treatment, the signal intensities of framework Al at 58 ppm (Fig. 6b) decrease significantly in 2.4Cu-0.1Na-SSZ-13 catalyst, accompanied with the obvious enhancement of five- and six-coordinated extra-framework Al signals at 35 and –5 ppm, respectively. It means significant dealumination occurs in 2.4Cu-0.1Na-SSZ-13 catalyst during hydrothermal aging even though the long-range ordering of zeolite can maintain well in XRD pattern. Fig. 6b clearly indicates that the signal intensities of framework Al near 58 ppm decrease significantly with the residual Na^+ content decreasing from 2.3% to 0.1%. However, for aged 2.4Cu-3.4Na-SSZ-13 catalyst, there is a strong broad shoulder peak at 52 ppm. This peak may be resulted from another four-coordinated Al according to ^{27}Al MQ MAS NMR (Fig. S4 in supplementary material). Obviously, these results confirm that Na^+ ions can stabilize framework Al in Al-rich Cu-SSZ-13 catalyst.

^1H MAS NMR was conducted to measure the Brönsted acidity for catalysts with different amount of residual Na^+ ions and the spectra are shown in Fig. 7. The peaks at 4.0, 2.5, and 2.0 ppm are attributed to Brönsted acid site, extra-framework AlOH and isolated silanol groups, respectively [30]. In the fresh catalysts, the amount of Brönsted acid sites decrease with the increase of the residual Na^+ . Even though 2.4Cu-3.4Na-SSZ-13 was directly prepared from the Cu ion exchange of Na-SSZ-13, there is still significant amount of Brönsted acid site, which may result from the generation of Brönsted acid site due to the auto-reduction of Cu^{2+} to Cu^+ during calcination or high temperature dehydration process [15,31,32]. It's worth noting when Na^+ amount is decreased to 0.6%, the amounts of AlOH and SiOH increase significantly due to the dealumination. It further confirms that Na^+ ions can stabilize framework Al even in as-prepared catalysts. After hydrothermal aging there is obvious loss of Brönsted acid site (Fig. 7b). The same trend that residual Brönsted acid site increase with the decrease of residual Na^+ is also observed in aged catalysts, and almost no remaining Brönsted acid site is observed in 2.5Cu-2.3Na-SSZ-13 and 2.4Cu-3.4Na-SSZ-13 catalysts.

UV-Vis-NIR spectra of fresh and hydrothermally aged samples acquired at ambient conditions are shown in Fig. 8. All spectra show peaks near 48000, 35000 and 12500 cm^{-1} represent $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$ charge transfer transitions, and the d–d transition of Cu^{2+} ions in an octahedral environment, respectively, and they are characteristic of the isolated Cu^{2+} [33,34]. It should be noted that these isolated Cu^{2+} ions observed in UV-Vis-NIR spectra could be the mobile aqueous complexes. The peaks near 22,500 and 40,000 cm^{-1} are attributed to the d–d transition and charge transfer transition of Cu with octahedral environment in CuO_x [34–36]. For the fresh catalysts, only 2.4Cu-3.4Na-SSZ-13 show weak peaks at 40,000 cm^{-1} of minor CuO_x . After hydrothermal aging the catalysts with Na^+ content above 2.3% show significant enhancement of the signal intensities of CuO_x at 22,500 and 40,000 cm^{-1} . Especially for 2.4Cu-3.4Na-SSZ-13, the significant increase of these signal intensities means severe aggregation of Cu species occurs in the catalyst. However, those of isolated Cu species at 12,500 cm^{-1} seem to be unchanged or even enhanced after hydrothermal treating. It could be due to the fact that the band intensity at 12,500 cm^{-1} is affected by the d–d transition probability, which is strongly determined by the coordination environment of Cu^{2+} ions [33,37,38]. For the hydrothermally aged samples the Cu^{2+} coordination state might be altered comparing to the fresh ones, resulting in this inconsistency.

H_2 -TPR experiments were further carried out to examine the Cu species in the fresh and aged Cu-Na-SSZ-13 catalysts, and the results are shown in Fig. 9. All the fresh catalysts show a broad reduction peak at 320–360 °C, and it shifts from 360 to 320 °C with

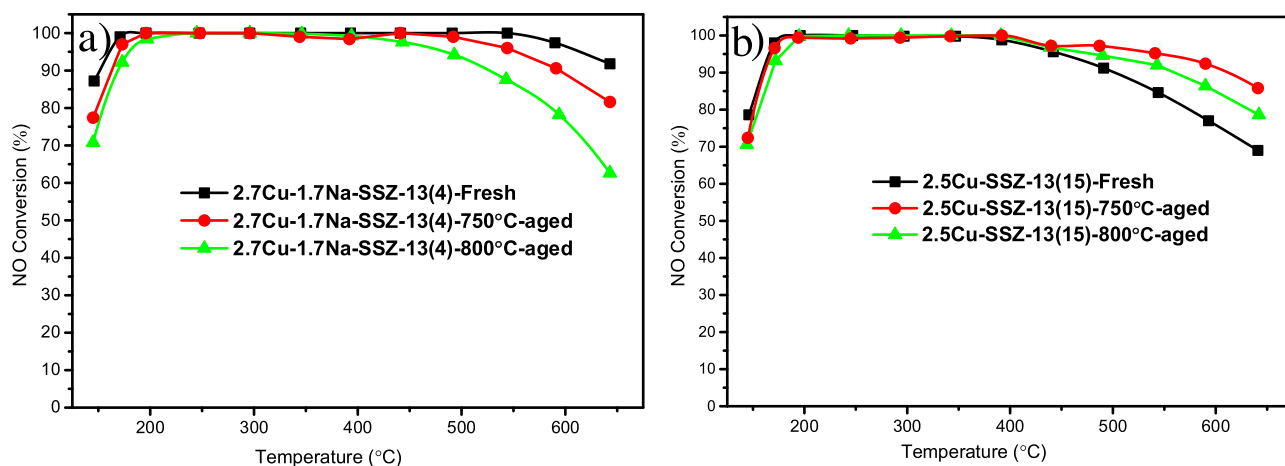


Fig. 4. NO conversions as a function of temperature for series hydrothermally aged catalysts: (a) 2.7Cu-1.7Na-SSZ-13(4) and (b) Commercial 2.5Cu-SSZ-13(15). Reaction Conditions: 500 ppm NO, 500 ppm NH₃, 10% O₂, 5% H₂O, balance N₂; GHSV = 80, 000 h⁻¹.

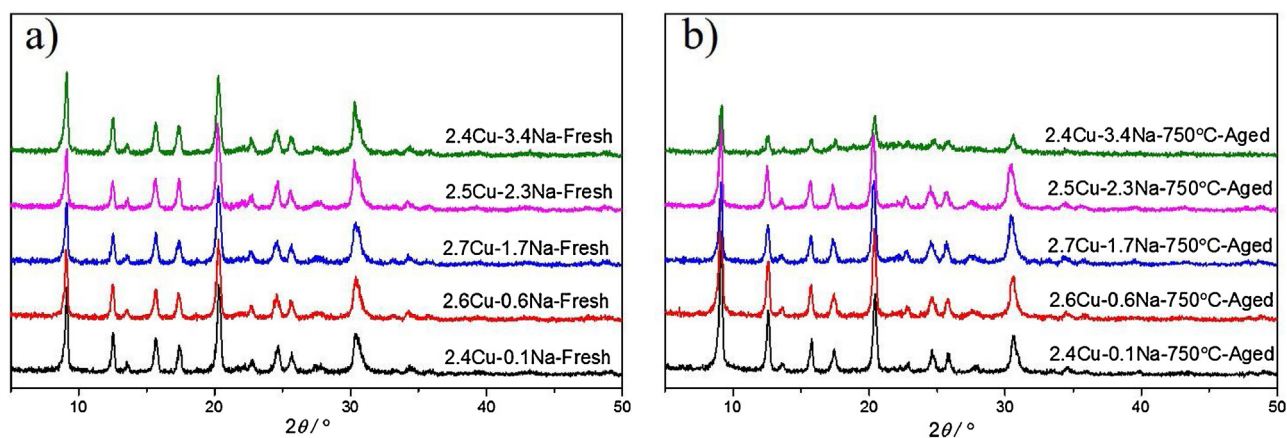


Fig. 5. XRD patterns of Cu-Na-SSZ-13(4) series catalysts: fresh (a) and hydrothermally aged (b).

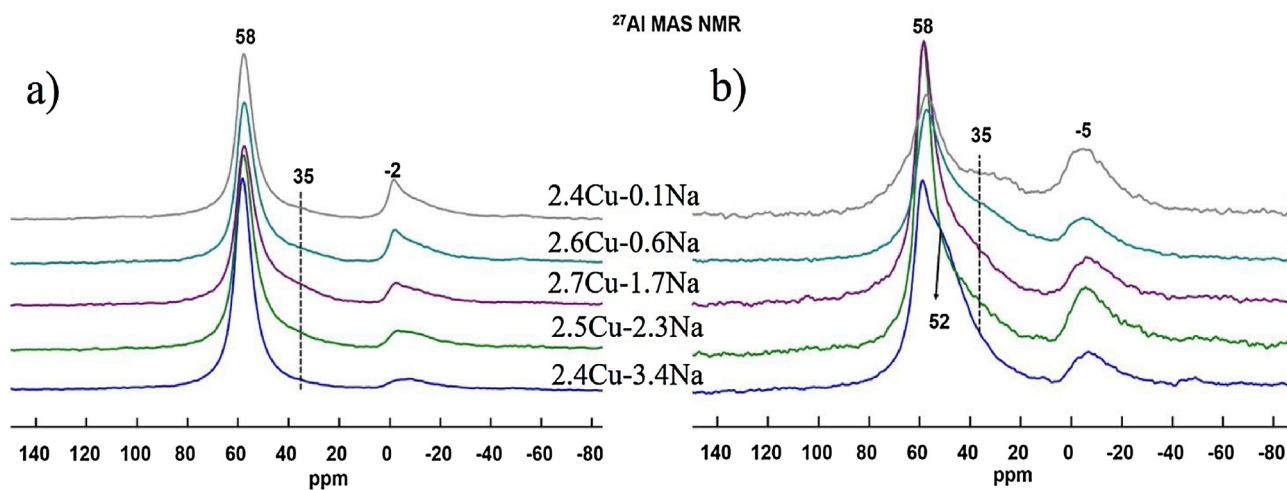


Fig. 6. ²⁷Al MAS NMR spectra of Cu-Na-SSZ-13(4) series catalysts: fresh (a) and hydrothermally aged (b).

the increase of Na⁺ content. This peak is attributed to the reduction of Cu²⁺ to Cu⁺ for the Cu²⁺ ions at 6-MR [14,39]. The shift of this reduction peak to lower temperatures clearly indicates that Na⁺ enhances the reducibility of Cu²⁺ ions [40]. When Na⁺ content is increased to 3.4%, the weak peak at 250 °C is attributed to the reduction of highly dispersed CuO_x, which is in accordance

with the appearance of 40,000 cm⁻¹ of CuO_x in UV-Vis-NIR spectra, and another strong peak at 460 °C is attributed to the reduction of Cu⁺ to Cu⁰ [17,39]. After hydrothermal treatment, the reduction peak of Cu²⁺ → Cu⁺ at 6-MR still exists and also shifts to lower temperature from 350 to 310 °C with the increase of Na⁺ content. When Na⁺ content is increased to 2.3%, the main reduction peak

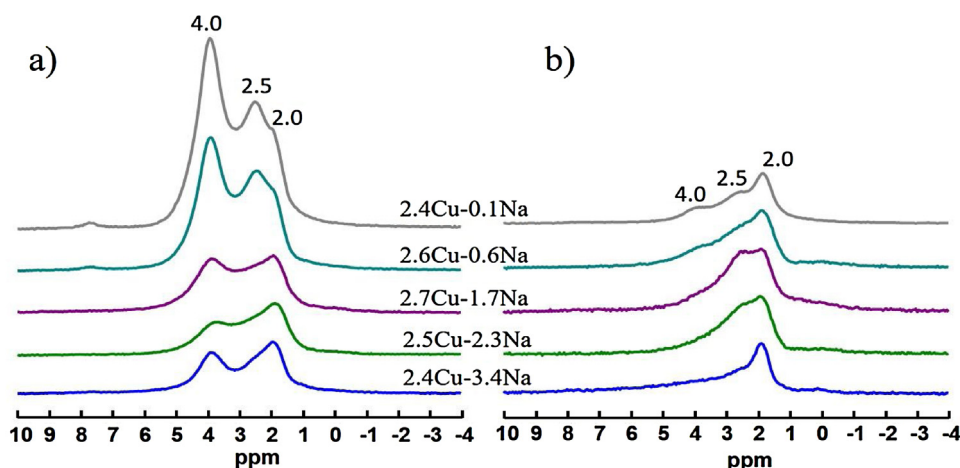


Fig. 7. ^1H MAS NMR spectra of Al-rich Cu-Na-SSZ-13(4) series catalysts: fresh (a) and hydrothermally aged (b).

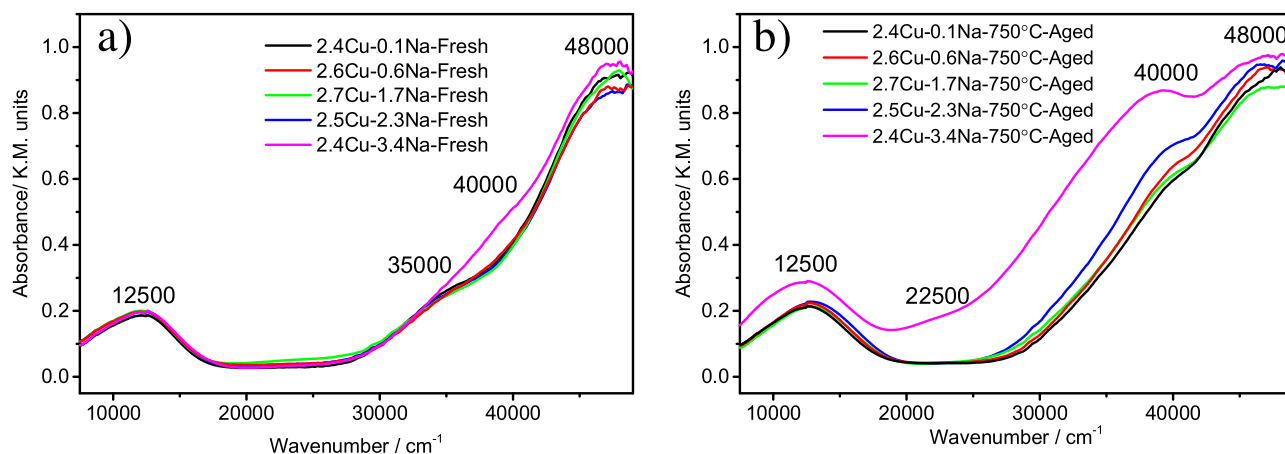


Fig. 8. UV-Vis-NIR spectra of Al-rich Cu-Na-SSZ-13(4) series catalysts: fresh (a) and hydrothermally aged (b).

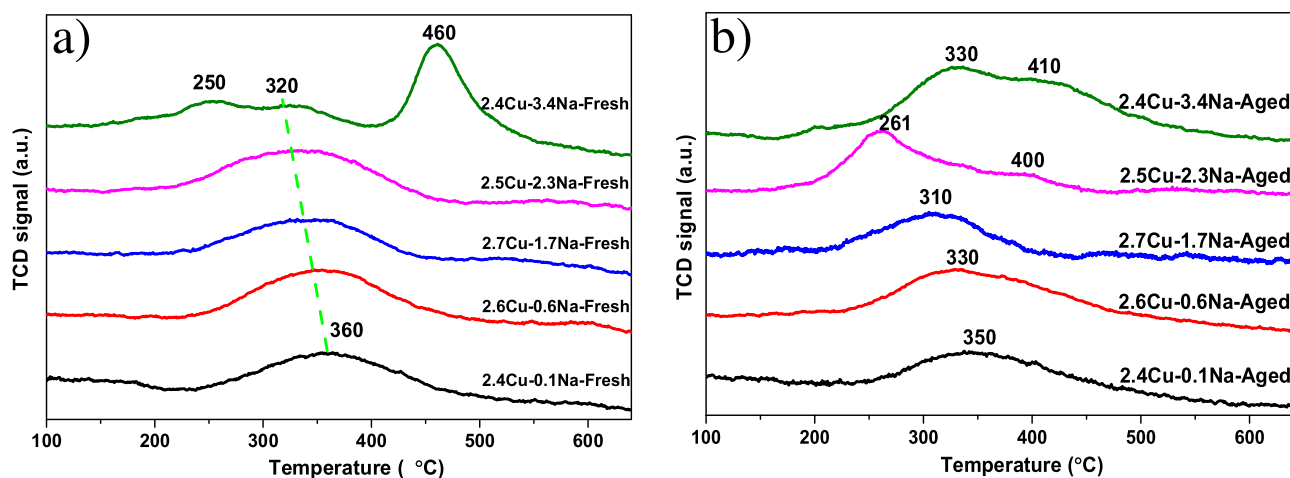


Fig. 9. H_2 -TPR profiles of Al-rich Cu-Na-SSZ-13(4) series catalysts: fresh (a) and hydrothermally aged (b).

at 261 °C may result from the reduction of highly dispersed CuO_x aggregates [17,39]. With further increase of Na^+ content to 3.4%, the broad reduction peaks near 330 and 410 °C are resulted from bulk CuO and CuAlO_x species, respectively [41–43]. H_2 -TPR profile (Fig. S5) of fresh 2.5Cu-SSZ-13(15) indicates the weak reduction peak of CuO_x aggregates at around 290 °C and extremely weak broad shoulder peak of $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ at around 350 °C. Comparing with Cu-

Na-SSZ-13(4), the relatively weak reduction peak means most Cu ions in 2.5Cu-SSZ-13(15) may be Cu^+ . After hydrothermal aging, the amount of CuO_x aggregates decreases accompanying with significant amount of Cu^{2+} and CuAlO_x . This agrees well with the enhancement of its high-temperature activity due to the decrease of CuO_x aggregates.

4. Discussion

The effect of Si/Al ratios on the NH_3 -SCR activities of Cu-SSZ-13 catalysts has been investigated by Gao and co-workers, and NO turn over frequency (TOF) was found to increase at both high and low reaction temperatures with decrease of Si/Al ratios due to the promotion effect of Brønsted acid sites [20]. When Cu exchange degree is very low and all the Cu species are in isolated Cu^{2+} state, the promotion effect of Brønsted acid sites play an important role in enhancement of the pre-exponential factor and/or storage of reactive NH_3 [20]. However, the definitions of TOF are based on the amount of total exchanged Cu without distinguishing the isolated Cu species, which is generally accepted as the active center in NH_3 -SCR reaction [8–11]. In our case, Cu exchanged Al-rich SSZ-13 zeolites from organotemplate-free synthesis show higher NO conversions than the conventional high-silica Cu-SSZ-13 catalysts with similar Cu loadings, which may be due to more isolated Cu species appeared. This is consistent with our findings in the NH_3 -SCR performances over Al-rich Cu- and/or Fe-Beta zeolites from organotemplate-free synthesis, and also confirmed by other groups [44–47]. When Na^+ ions are introduced, it seems that they can further enhance NH_3 -SCR activities at low temperatures (Fig. 2) with the exception of 2.4Cu-3.4Na-SSZ-13(4) probably due to the formation of CuO_x identified by the band at $40,000\text{ cm}^{-1}$ in UV-Vis-NIR spectrum (Fig. 8a). Even though introduction of Na^+ can enhance the reducibility of Cu^{2+} (Fig. 9a), previous kinetic analysis indicates that Cu active center has the same activation energy with or without Na^+ ions, and introduction of co-cation was claimed to alter the pre-exponential factor and/or storage of reactive NH_3 according to the Arrhenius equation [21,40]. Considering NH_3 -SCR reaction at low temperatures, most of Brønsted acid sites will adsorb NH_3 to easily form NH_4^+ , while NH_4^+ is not active for NH_3 -SCR reaction [48]. Na^+ ions promotion effect may result from the different ammonia adsorption capability between NH_4^+ and Na^+ ions, and Na^+ type zeolite adsorbs more NH_3 than NH_4^+ type counterpart reported from previous NH_3 -TPD results [21,49]. As displayed in Fig. S6, NH_3 -TPD profiles of as-prepared Cu-Na-SSZ-13(4) clearly demonstrate that the amount of NH_3 with desorption peak at ca. 195°C increases with Na^+ contents. This confirms that introduction of Na^+ increases the storage of weakly adsorbed NH_3 , which may result in the enhancement of low-temperature activity. It is also consistent with what Gao et al. found in Refs. [20,21]. With respect to high-temperature activity, NO conversion loss is mainly resulted from the side-reaction of non-selective NH_3 oxidation, and Cu ions aggregate into CuO_x is a major contribution [16,17,41]. It is reasonable that introduction of more Na^+ ions will make Cu ions ready to aggregate into CuO_x , which becomes more obvious in the aged catalysts (Fig. 8b). Even at moderate Na^+ content, i.e. 2.7Cu-1.7Na-SSZ-13(4) catalyst, there is an enhancement of the band at $40,000\text{ cm}^{-1}$ in UV-Vis-NIR spectrum from clustered CuO_x after hydrothermal aging at 750°C (Fig. 10). If with more severely aged at 800°C , more CuO_x clusters appear, and thus shows prompt decrease of high-temperature NH_3 -SCR activity (Fig. 4a). Whereas, 2.4Cu-0.1Na-SSZ-13(4) catalyst with the least Na^+ content has the best high-temperature NO conversions as Cu ions maintain well in isolated status even after hydrothermal aging (Figs. 8b, 9b).

The hydrothermal stability of Cu-SSZ-13 is mainly influenced by two factors: (1) the stability of zeolitic framework; (2) the stability of Cu ions. In conventional high-silica SSZ-13 zeolite, the framework Al is relative stable. However, in Al-rich SSZ-13 zeolite, the framework Al is very susceptible to dealumination. Once dealumination occurs, the produced silanol defects will significantly affect the hydrothermal stability [25]. ^{27}Al and ^1H MAS NMR indicates when Na^+ is introduced, most 4-coordinated framework Al are preserved with minor silanol and AlOH groups. These results clearly indicate Na^+ ions can stabilize the framework Al. However, intro-

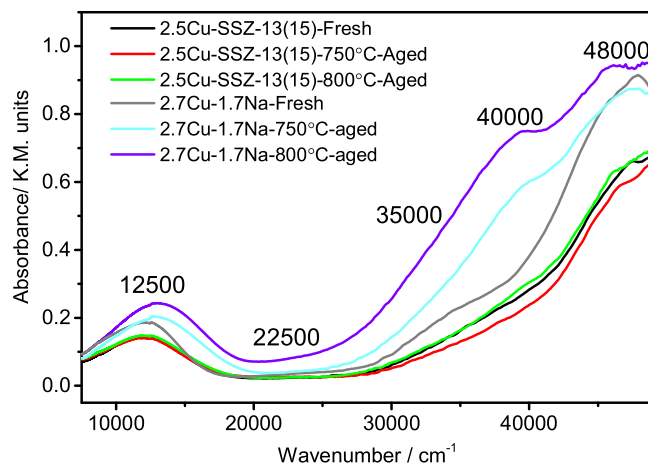


Fig. 10. UV-Vis-NIR spectra of hydrothermally aged 2.7Cu-1.7Na-SSZ-13(4) and commercial 2.5Cu-SSZ-13(15) catalysts.

duction of Na^+ will weaken the interaction between Cu ion and zeolite, and enhance the reducibility of Cu ions as shown by H_2 -TPR in Fig. 9 [21]. Therefore, during high-temperature hydrothermal aging, Cu ions will be inclined to aggregate into CuO_x . The formation of CuO_x will further destruct the zeolite structure and react with extra-framework Al producing CuAlO_x . As a result, the 2.4Cu-3.4Na-SSZ-13(4) with the highest Na^+ content shows significant amount of aggregated CuO_x and CuAlO_x species in UV-Vis-NIR spectra and severe destruction of zeolite crystallinity. Although significant dealumination occurs in aged 2.4Cu-0.1Na-SSZ-13 catalyst, it still has the long-range order crystallinity and most Cu species will maintain in the isolated state due to strong interaction between Cu ions and zeolite. On the other hand, as is previously reported the stability of Cu ions is also affected by the amount of Cu ion due to different locations of Cu^{2+} at 6-MR or CHA cage [17]. When too much amount of Cu ions exist, Cu ions in CHA cage will be also inclined to form CuO_x , and decrease the hydrothermal stability. In our case, 2.5% Cu corresponds to $\text{Cu}/\text{Al}=0.13$, and the Cu ion exchange degree is only about 25% assuming each Cu^{2+} occupies two ion exchange sites. It can be safely concluded that all Cu ions should be in 6-MR for the most stable site. Therefore, the low hydrothermal stability of Cu-Na-SSZ-13 catalysts with excess amount of Na^+ ions may result from the fact that the interaction between Cu ions and zeolitic framework is significantly weakened.

5. Conclusions

Cu-exchanged Al-rich SSZ-13 catalysts with Si/Al=4 from organotemplate-free synthesis have been prepared and tested in the NH_3 -SCR reaction. Compared with conventional high-silica SSZ-13, Al-rich Cu-SSZ-13 catalysts show better NH_3 -SCR performance with NO conversions above 85% at wide-temperature window ranging from 150 to 650°C . Preserving part of Na^+ ions in the as-prepared Na-SSZ-13 through partial ion exchange can improve both the low-temperature activity and its hydrothermal stability of Al-rich Cu-SSZ-13 catalyst. ^{27}Al and ^1H MAS NMR indicate that more framework Al can be preserved with the increase of residual Na^+ to 2.3% in the fresh or hydrothermally aged catalysts. UV-Vis-NIR combined with H_2 -TPR demonstrate that Na^+ co-cations enhance the reducibility of Cu^{2+} at 6-MR. However, excess amount of Na^+ ions weaken the interaction between Cu ion and zeolitic framework, and result in the formation of CuO_x during hydrothermal treatment, which is detrimental to high temperature activities and decreases the hydrothermal stability of Al-rich Cu-SSZ-13 catalysts. The optimized Al-rich 2.7Cu-1.7Na-SSZ-13

catalyst exhibits NH_3 -SCR performance on par with the commercial high-silica catalyst at 150–550 °C after 750 and 800 °C hydrothermal aging, and shows promising potential application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.06.013>.

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